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PC10 PC8CG2H 5D1A 5D1Y 5DY 5G1A 5G1Y 5G2B 5G2G1 5G2G4
5G2G5 5G2GY 5G2Y 5G3 5GY 5Y(54) A TONER FOR DEVELOPING ELECTROSTATIC
LATENT IMAGES

(71) We, KONISHIROKU PHOTO INDUSTRY CO., LTD., a Corporation organized and existing under the laws of Japan, of 1—10, 3-chome, Nihonbashi-Muro-machi, Chuo-ku, Tokyo, Japan, and SEKISUI KAGAKU KOGYO KABUSHIKI KAISHA, a Corporation organized and existing under the laws of Japan, of No. 2, Kinugasa-cho, Kita-ku, Osaka, 530-Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a toner for developing electrostatic latent images in electrophotography, electrostatic recording, electrostatic printing and the like.

The process of developing electrostatic latent images is roughly divided into two types; namely a liquid developing method using a developer formed by finely dispersing a pigment or dye into an insulating organic liquid, and a dry developing method using a fine powder developer, namely a so-called toner formed by dispersing a colorant such as carbon black into a natural or synthetic resin. The latter dry developing method includes a cascade method, a fur brush method, a magnetic brush method, an impression method, and a powder cloud method. The invention relates to a toner for use in the latter dry developing method.

The fixation is generally accomplished by fusing the toner. Fixation can be conducted immediately after development, where permanent images are formed on a photosensitive material or other electrostatic recording material, or after image transfer which is subsequent to the development, where permanent images are formed on a transfer sheet. At this fixation, fusion of the toner image is performed either by contacting the toner image with a vapor of a solvent or by heating the toner image. As the heating

method, there are generally adopted a non-contact heating method using an electric furnace and a press heating method using a heated roller.

According to the press heating method using a heated roller, there is employed a heated roller having a surface composed of a material having a releasing property to the toner and the roller is contacted with a sheet on which an image is to be fixed so that it has a pressing contact with the toner image surface, whereby fixation is accomplished. In this heating method, which is generally called "a heated roller fixing method", since the surface of the heated roller comes into a pressing contact with the toner image-carrying surface of a sheet on which the toner image is to be fixed, a good thermal efficiency can be attained in fusing the toner image to the fixing sheet and fixation can be accomplished very promptly. Therefore, this fixing method is utilized very advantageously for electrophotographic copying machines of the transfer type in which high speed reproduction is intended. In this case, however, since the surface of the fixing roller is press-contacted with the toner image, a part of the toner image adheres to the fixing roller surface and is re-transferred to a subsequent fixing sheet, causing a so-called offset phenomenon and sometimes staining the fixing sheet. Therefore, in the heated roller fixing method, it is one of the indispensable requirements that the roller surface should have such a property that the toner does not adhere to it.

As means for preventing a toner from adhering to the surface of a fixing roller, there has been adopted a method in which a roller having a surface composed of a material having a good releasing property to the toner, such as a fluorine-containing resin, is used and an offset-preventing liquid such as a silicone oil is fed to the surface of the roller to cover the roller surface with a liquid film.

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This method is effective for preventing occurrence of the toner offset phenomenon, but an unpleasant smell is generated because the offset-preventing liquid is heated, and since it is necessary to provide an apparatus for feeding the offset-preventing liquid, the mechanism of the copying machine is complicated and the cost of the copying machine in which a high accuracy is required for obtaining good results stably becomes high. However, since the toner adheres to the surface of the fixing roller and causes the offset phenomenon if no offset-preventing liquid is fed, despite the foregoing disadvantages, feeding of an offset-preventing liquid cannot be avoided.

It is therefore a primary object of this invention to provide a toner for developing electrostatic latent images which makes it possible to perform the heated roller fixation at a high efficiency without occurrence of the offset phenomenon to the surface of which no offset-preventing liquid is fed, even when a fixing roller, is employed.

We have found that the above object can be attained by a toner for developing electrostatic latent images comprising a colorant and a main resin based on an α,β - ethylenically unsaturated monomer and having a weight average molecular weight (M_w)/number average molecular weight (M_n) ratio (M_w/M_n ratio) of from 3.5 to 40, measured as herein-after defined.

When the toner of this invention for developing electrostatic latent images is employed, even if an offset-preventing liquid is not fed to the surface of a fixing roller, the heated roller fixation can be accomplished at a high efficiency without occurrence of the offset phenomenon. Therefore, if the toner of this invention is employed, the mechanism of the fixing device can be simplified, and in a high speed copying machine provided with such simplified fixing device, the accuracy, operation stability and reliability can be highly improved and the cost of the copying machine can be reduced. Thus, according to this invention, there is attained an advantage that design of a super-high speed copying machine can be facilitated.

In general, toners comprise a resin component, a coloring component composed of a pigment or dye, a plasticizer and additives for adjusting physical properties and developing characteristics of the toner, such as a charge-controlling agent. Natural or synthetic resins are used singly or in blends as the resin component. In some cases, it is possible to use as the resin component a colored polymer containing a dye bonded to the polymer chain.

The toner of this invention for developing electrostatic latent images comprises a resin containing as a structural unit derived from an α,β - ethylenically unsaturated monomer

and having a weight average molecular weight to number average molecular weight ratio (referred to as M_w/M_n ratio hereinafter and measured as hereinafter defined) of from 3.5 to 40, (hereinafter referred to as "the resin of this invention") as the main resin component. In short, the toner of this invention is characterized in that it comprises the above-mentioned resin as a main resin component. More specifically, when the resin of this invention is incorporated into a toner in an amount of at least about 60% by weight, preferably at least 75% by weight, based on the total resin component of the toner, the remainder being constituted by up to 40% by weight, based on total resin, of a second resin containing no units derived from an α,β - ethylenically unsaturated monomer, occurrence of the offset phenomenon of the toner to a heating fixing roller can be effectively prevented.

The first characteristic of the resin of this invention is that it comprises an α,β - ethylenically unsaturated monomer as a main structural component. The resin of this invention may be a homopolymer composed of one monomer alone or a copolymer composed of two or more monomers. Further, the resin of this invention may be a polymer blend comprising two or more of such homopolymers and or copolymers.

The second characteristic of the resin of this invention is that the M_w/M_n ratio is within the range of from 3.5 to 40. When the resin of this invention is composed of one homopolymer or copolymer, the value of the above ratio is that of said homopolymer or copolymer, and when the resin of this invention is a polymer blend, said value is the value of the polymer blend as a whole. More specifically, in the case of a polymer blend, it is not absolutely necessary that the value M_w/M_n should be from 3.5 to 40 in each of constituent polymers but it is sufficient that the value M_w/M_n of the polymer blend as a whole is from 3.5 to 40.

As the α,β - ethylenically unsaturated monomer to be used as the constituent of the resin of this invention, there can be mentioned, for example, styrene monomers such as styrene, o - methylstyrene, m - methylstyrene, p - methylstyrene, α - methylstyrene, p - ethylstyrene, 2,4 - dimethylstyrene, p - n - butylstyrene, p - tert - butylstyrene, p - n - hexylstyrene, p - n - octylstyrene, p - n - nonylstyrene, p - n - decylstyrene, p - n - dodecylstyrene, p - methoxystyrene, p - phenylstyrene, p - chlorostyrene and 3,4 - dichlorostyrene; vinylnaphthalenes; mono - olefins such as ethylene, propylene, butylene and isobutylene; vinyl halides such as vinyl chloride, vinyl bromide, and vinyl fluoride; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate and vinyl butyrate; α - methylene aliphatic monocarboxylic acid

esters such as methyl acrylate, ethyl acrylate, n - butyl acrylate, isobutyl acrylate, propyl acrylate, n - octyl acrylate, dodecyl acrylate, lauryl acrylate, 2 - ethylhexyl acrylate, stearyl acrylate, 2 - chloroethyl acrylate, phenyl acrylate, methyl α - chloroacrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n - butyl methacrylate, isobutyl methacrylate, n - octyl methacrylate, dodecyl methacrylate, lauryl methacrylate, 2 - ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate; acrylic acid and methacrylic acid derivatives such as acrylonitrile, methacrylonitrile and acrylamide; vinyl ethers such as vinylmethyl ether, vinyl ethyl ether and vinylisobutyl ether; vinyl ketones such as vinylmethyl ketone, vinylhexyl ketone and methylisopropenyl ketone; and N - vinyl compounds such as N - vinylpyrrole, N - vinylcarbazole, N - vinylindole and N - vinylpyrrolidine. The resin of this invention includes those formed by acetalizing polymers, such as polyvinyl acetals, e.g., polyvinyl butyral. Among these monomers, aromatic vinyl monomers and α - methylene aliphatic monocarboxylic acid esters are especially preferred, and especially good effects can be obtained when resins containing such monomers as the main structural component are employed in this invention. Moreover, a resin containing monomers of the foregoing two types in which the styrene type monomer content is at least 30 mole % is especially preferred, because such resin is excellent in not only the offset-preventing effect but also the properties required of the toner at the manufacturing steps, such as the triboelectric property, the pulverizing property and the uniform additive dispersibility.

In the resin of this invention, the value of the M_w/M_n ratio is within a range of from 3.5 to 40, and it is preferred that the number average molecular weight be within a range of from 2000 to 30000. Values of M_w , M_n and M_w/M_n can be measured by various methods and the determined values differ to some extent depending on measuring methods. Accordingly, each of the values of M_w , M_n and M_w/M_n is defined as one measured according to the following method.

In short, each value is determined under the following conditions according to gel permeation chromatography. At a temperature of 25°C., a solvent (tetrahydrofuran) is flown at a rate of 1 ml per minute, and a solution of tetrahydrofuran containing 0.4 g/dl of the sample is poured in an amount of 8 mg as the sample. In this state, the measurement is conducted. A calibration line showing the relationship between molecular weight and elution volume (count number) is obtained by use of standard samples of singly dispersed polystyrenes. The measurement of samples to

be tested is carried out within a range where the calibration line is straight. Reliability of this measurement is confirmed from the fact that the M_w/M_n of a standard sample of polystyrene NBS 706 ($M_w=28.8 \times 10^4$; $M_n=13.7 \times 10^4$; $M_w/M_n=2.11$) as measured by the above manner is 2.11 ± 0.10 .

The toner for developing electrostatic latent images including the above mentioned resin of this invention as the main resin component is characterized in that not only does it cause no offset phenomenon but also the range of the fusing temperature where no offset phenomenon is caused is very broad. Because of this characteristic, the toner is hardly influenced by changes in the temperature at the fixing step and design of the fixing device can be greatly facilitated.

As pointed out hereinabove, the intended object of this invention can be attained by using a resin having an M_w/M_n ratio ranging from 3.5 to 40, but an especially high offset-preventing effect can be attained when a resin having an M_w/M_n ratio of from 4.0 to 30 is employed.

In preparing toners, after the resin component has been compounded with a coloring component and additives, the kneading step using a kneader is generally carried out. A massive toner composition obtained by the kneading treatment is then pulverized and sieved to collect a toner having a desired particle size. Toner particles removed by the sieving treatment are kneaded again by means of a kneader, followed by pulverizing and sieving. The overall yield is increased by repeating the above procedures. However, since a shearing force is imposed on the resin component of the toner at the kneading step using a kneader, the main chain of the resin is cut to change the structure and molecular weight of the resin. Even when the molecular weight of the resin is changed more or less by the first kneading operation, if the M_w/M_n value is maintained within a range of from 3.5 to 40, the intended object of this invention can be attained, but while the kneading operation is repeated as mentioned above so as to increase the yield, it sometimes happens that the molecular weight of the resin is gradually changed to such an extent that the M_w/M_n value is reduced below 3.5 or it is increased beyond 40. In such case, a toner capable of attaining the object of this invention cannot be obtained at all, and therefore, the yield of the intended toner is decreased. Increase of the yield is one of important factors in the production of toners. Among resins of this invention, those having an M_w/M_n ratio ranging from 4.0 to 30 are especially preferred. More specifically, since in such resins the above value is hardly deviated from the range of 3.5 to 40 even if the kneading operation is repeated, there is attained an advantage that the yield of the

toner can be greatly improved. Also in view of this fact, use of a resin having an M_w/M_n value of from 4.0 to 30 is especially preferred.

Especially good results are obtained when the resin of this invention has a softening point of 100 to 170°C. as measured according to the Ball and Ring method, though the preferred softening point varies to some extent depending on the kind of the monomer included as the resin constituent and other factors. Moreover, use of a resin having a glass transition point of 40 to 110°C. is especially effective. When the resin of this invention has a softening point lower than 100°C. the resin tends to be excessively pulverized and a photoconductive photo-sensitive plate is readily stained by the toner filming. When the softening point of the resin exceeds 170°C. pulverization is made difficult because of the hardness of the resin and a large amount of heat is required at the fixing step, causing the defect of a low fixing efficiency. When the glass transition point of the resin is lower than 40°C., since the toner is generally stored at a temperature lower than 40°C., agglomeration of the toner particles is caused to occur during storage by the cold flow phenomenon. When the glass transition point of the resin exceeds 110°C., if the material of the fixing roller is other than a metal, for example, polytetrafluoroethylene, the roller material is readily worn away at temperatures higher than 250°C. and is decomposed at such temperatures. Therefore, there is brought about a disadvantage that elevation of the fixing temperature is limited by the roller-constituting material and the fixation cannot be accomplished sufficiently when the fixation is conducted at a high speed.

Incidentally, there is observed a tendency that as the value M_w/M_n becomes great, the glass transition point of the resin comes to have a certain range and does not show a certain specific value, and in some resins having a great M_w/M_n value, it is difficult to measure the glass transition point.

The toner of this invention for developing electrostatic latent images comprises the above-mentioned resin of this invention as a main resin component, and the resin component of the toner of this invention may either be composed of the resin of this invention alone or further comprise other polymer or resin according to need. As resins that can be used in combination with the resin of this invention, there can be mentioned resins containing no α,β -ethylenically unsaturated monomer units as a monomer component, for example, non-vinyl resins such as rosin-modified phenol-formalin resins, epoxy resins, polyurethane resins, cellulose resins and polyether resins. The kind and amount of such additional resin are chosen and determined appropriately depending on

the kind of the resin of this invention, the kind of the monomer constituting the resin of this invention, the copolymerization ratio of monomers when the resin of this invention is a copolymer, the molecular weight of the resin of this invention, the softening point of the resin of this invention, the glass transition point of the resin of this invention and the like, so as to impart desired physical properties and developing characteristics to the resulting toner. For example, though the resin of this invention to be used as the main resin component of the toner is sufficient in the offset-preventing effect, it sometimes happens that it is insufficient or defective in that the toner is too soft to impart a sufficient pulverizing property at the toner-preparing steps or show a sufficient triboelectric property or the resin fails to provide a toner of good properties such as stability and resistance to agglomeration. In such case, incorporation of a xylene resin is effective for overcoming such disadvantages and providing a toner having good quality. Further, if the main component of the toner is composed solely of a polystyrene resin included in the scope of this invention, the resin is too brittle and readily super-pulverized. In such case, incorporation of an epoxy resin is effective for overcoming this disadvantage.

Synthesis of the resin of this invention will now be described.

When a customary polymerization method is adopted, a resin having an M_w/M_n ratio of from 1.5 to 3.0 is generally obtained. Resins of an M_w/M_n ratio of from 3.5 to 40 to be used in this invention can be synthesized according to methods such as described below. According to one method, the polymerization is carried out while changing the polymerization temperature continuously or intermittently. According to another method, the polymerization is carried out by charging successively several kinds of monomers differing in the initiator concentration or the chain transfer agent concentration. A resin having a higher M_w/M_n ratio can easily be obtained by incorporating a resin having a high molecular weight into a resin having a relatively low molecular weight. In these methods, the polymerization can be performed according to any of the bulk polymerization process, the solution polymerization process, the suspension polymerization process, the emulsion polymerization process and the like. In view of the easiness in handling the resulting resin and the reduction of the production cost, it is preferred that the polymerization be carried out according to the suspension polymerization process. As means for increasing the M_w/M_n value, there can be mentioned a method in which several kinds of resins differing in molecular weight are dissolved in a solvent and the solvent is removed

by drying under reduced pressure or spray drying and a method in which several kinds of resins differing in molecular weight are heated and molten to dissolve them into one another and form a resin blend. In order to obtain the intended effects of this invention, it is preferred that resin components be uniformly dispersed to form a homogeneous system.

Synthesis of a typical instance of the resin of this invention will now be illustrated by reference to the following Synthesis Example.

Synthesis Example

0.1 g of a partially saponified polyvinyl alcohol (Gosenol GH-17 manufactured by Japanese Synthetic Rubber) was charged in a separable flask having a capacity of 1 liter, and dissolved in 100 ml of distilled water. Then, a monomer mixture A indicated in the following Table was added to the solution to suspend and disperse the mixture in the solution. The atmosphere was replaced by

nitrogen gas and the temperature was elevated at 80°C. At this temperature polymerization was carried out for 15 hours. The reaction mixture was cooled to 40°C., and a monomer mixture B indicated in the following Table was added to the reaction mixture and the mixture was agitated at 40°C. for 2 hours. Separately, an aqueous solution of 0.4 g of a partially saponified polyvinyl alcohol (Gosenol GH-17) in 100 ml of distilled water was prepared. The so formed aqueous solution was added to the above suspension. Then, the temperature was elevated again to 80°C. and this temperature was maintained for 8 hours to effect the polymerization. Then, the temperature was further elevated at 95°C. and this temperature was maintained for 2 hours to complete the polymerization. The reaction product was cooled, dehydrated, washed repeatedly and dried to obtain a resin in which the M_w/M_n ratio was 5.4, the M_n value was 1.1×10^4 and the softening temperature as measured according to the ball and ring method was $140 \pm 2^\circ\text{C}$.

Monomer	Monomer Mixture A	Monomer Mixture B
styrene	5 g	50 g
methyl methacrylate	2 g	20 g
butyl methacrylate	3 g	30 g
benzoyl peroxide	0.02 g	2 g
α - methylstyrene (dimer)	—	3 g

The α - methylstyrene (dimer) used was a mixture of 2,4 - diphenyl - 4 - methyl - 1, - pentene and 2,4 - diphenyl - 4 - methyl - 2 - pentene synthesized according to the disclosure of the specification of U.S. Patent No. 2,429,719 and a fraction having a refractive index of 1.569 was employed.

In the toner of this invention for developing electrostatic latent images, an optional appropriate pigment or dye is used as a colorant. For example, there can be employed carbon black, Nigrosine dyes, Aniline Blue, Chalco Oil Blue, Chrome Yellow, Ultramarine Yellow, Du Pont Oil Red, Quinoline Yellow, Methylene Blue Chloride, Phthalocyanine Blue, Malachite Green Oxalate, lamp black, Rose Bengal, and mixtures thereof. It is necessary that such colorant should be incorporated in an amount enough to color the toner so that a visible image can be obtained.

In the toner of this invention for developing electrostatic latent images, occurrence of the offset phenomenon of the toner can be effectively prevented by using the resin of this invention as the main resin component of the toner. In order to further enhance the offset-preventing effect, if desired, it is possible to incorporate into the toner a compound having releasing properties. As such compounds, there can be mentioned, for example, metal salts of fatty acids such as

cadmium stearate, barium stearate, lead stearate, nickel stearate, cobalt stearate, copper stearate, strontium stearate, calcium stearate, magnesium stearate, zinc oleate, manganese oleate, iron oleate, cobalt oleate, copper oleate, lead oleate, magnesium oleate, zinc palmitate, cobalt palmitate, copper palmitate, magnesium palmitate, aluminum palmitate, calcium palmitate, zinc linolate, cobalt linolate, calcium linolate, zinc ricinoleate, cadmium ricinoleate, lead caprylate and lead caproate; higher fatty acids having at least 28 carbon atoms; natural and synthetic paraffins; fatty acid esters and partially saponified products thereof; and alkylene - bis - fatty acid amides such as ethylene - bis - stearoyl amide. These compounds are used singly, or two or more of them are combined appropriately. Such compound is incorporated in the toner in an amount of 0.1 to 10 parts by weight, preferably 0.5 to 5 parts by weight, per 100 parts by weight of the resin component of the toner. By incorporation of such compound, the dispersibility of other toner additives such as a colorant and a charge-controlling agent into the resin component can be improved. Further, in case the resin component is relatively brittle, the incorporation of such compound prevents excessive pulverization at the grinding step in the toner-preparing process, and hence, a toner of a desired particle size can be obtained in a

high yield. Moreover, such releasing property-imparting compound exhibits effects of increasing the stability of the toner, preventing the change of the triboelectric property even in extended use and prolonging the life of the toner.

The resin of this invention may be used as the resin component of a toner for use in a development, where a developer consists of the toner containing a magnetic material.

In such toner, the magnetic material serves as a colorant.

According to need, the toner of this invention for developing electrostatic latent images may further comprise other various toner additives such as a charge-controlling agent and a plasticizer.

A toner image formed on a fixing sheet by using the toner of this invention for developing electrostatic latent images can be conveniently fixed on the fixing sheet at a high efficiency without occurrence of the undesired offset phenomenon according to the heated roller fixing method even when a fixing roller of the type where an offset-preventive liquid is not fed to the surface of the roller is employed. Fixing rollers having a smooth surface composed of a fluorine resin such as polytetrafluoroethylene, FEP (manufactured by Du Pont), Fluon (manufactured by ICI), Kel F (Registered Trade Marks) (manufactured by 3M) and Daifuron (manufactured by Daikin) or a relatively hard silicone rubber such as KE-1300 RTV (manufactured by Shinetsu Kagaku) are effectively employed for the heating roller fixing treatment. In some case, a fixing roller having a metal surface can be effectively employed.

This invention will now be described in detail by reference to the following Examples that by no means limit the scope of this invention. In the Examples, all of "parts" are by weight unless otherwise indicated.

Example 1

100 parts of polystyrene (A) [$M_w/M_n=3.7$; $M_n=9600$; softening point as measured according to the ball and ring method (hereinafter referred to as "B & R")= $120\pm 2^\circ\text{C}$.; glass transition point (hereinafter referred to as "Tg")= 97°C .] was mixed with 6 parts of Peares 155 (carbon black manufactured by Columbia Carbon) and 3 parts of Nigrosine Base EX (Nigrosine dye manufactured by Orient Kagaku), and the mixture was treated in a ball mill for about 24 hours and kneaded with a hot roll. Then, the mixture was cooled and pulverized to obtain a toner sample of this invention having an average particle size of about 13 to 15 microns. The above procedures were repeated in the same manner by using instead of the polystyrene (A) polystyrene (B)

($M_w/M_n=2.6$; $M_n=12000$;

B & R= $125\pm 2^\circ\text{C}$.; Tg= 97°C .),

to obtain a comparative sample.

4 parts each of the so obtained toner samples were mixed separately with 96 parts of an iron powder carrier having an average particle size of about 50 to about 80 microns to form 2 kinds of developers. Electrostatic latent images formed by a customary electrophotographic method were developed with these two toners respectively, and the resulting toner images were transferred on to transfer sheets and fixed by fusing the toner images by a pressing contact with a fixing roller having a surface composed of FEP, which was maintained at 165 to 175°C . In order to examine whether or not the fixed toner was re-transferred to the roller surface to cause the offset phenomenon, just after completion of the fixing operation transfer sheets free of a toner image were caused to have a pressing contact with the roller under the same conditions as above, and it was checked whether or not the transfer sheets were stained by the offset phenomenon.

As a result, it was found that when the comparative toner sample was used, the transfer sheet was conspicuously stained by the offset phenomenon of the toner, whereas in the case of the sample toner of this invention the transfer sheet was not stained at all and it was confirmed that the offset phenomenon was not caused to occur at all.

Example 2

Two toners were prepared in the same manner as Example 1 except that polystyrene (A1)

($M_w/M_n=4.5$; $M_n=8300$;

B & R= $125\pm 2^\circ\text{C}$.; Tg= 97°C .)

and polystyrene (A2)

($M_w/M_n=25$; $M_n=1900$;

B & R= $125\pm 2^\circ\text{C}$.; Tg= $-$)

were used separately instead of the polystyrene (A) used in Example 1.

The offset characteristics of these toners were examined in the same manner as in Example 1 except that a fixing roller having a surface composed of Daifuron was used as the fixing roller and the fusing temperature was changed to 180 to 190°C . It was confirmed that in each of the two samples the offset phenomenon was not caused at all.

Example 3

100 parts of a styrene (70 parts)-butyl methacrylate (30 parts) copolymer (A)

($M_w/M_n=4.6$; $M_n=17000$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=74^\circ\text{C}$.)

was mixed with 5 parts of Dia Black SH (carbon black manufactured by Mitsubishi Kasei) and 2.5 parts of Oil Black BW (Nigrosine dye manufactured by Orient Kagaku), and the mixture was treated in the same manner as in Example 1 to obtain a toner sample of this invention. The above procedures were repeated similarly by using instead of the copolymer (A) a styrene (70 parts) butyl methacrylate (30 parts) copolymer

($M_w/M_n=3.0$; $M_n=23000$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=74^\circ\text{C}$.),

to obtain a comparative toner.

The offset characteristics of these two toners were examined in the same manner as in Example 1 except that the fusing temperature was changed to 200 to 210°C . In the case of the comparative sample, the offset phenomenon was observed, but in the case of the toner sample of this invention it was confirmed that the offset phenomenon was not caused to occur at all.

Example 4

100 parts of a styrene (50 parts)-methyl methacrylate (20 parts)-butyl methacrylate (30 parts) copolymer (A1)

($M_w/M_n=5.4$; $M_n=11000$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=72^\circ\text{C}$.)

was mixed with 5 parts of Dia Black SH and 2 parts of Oil Black BW and the mixture was treated in the same manner as in Example 1 to obtain a toner sample of this invention. The above procedures were repeated in the same manner by using instead of the copolymer (A1) a styrene (50 parts)-methyl methacrylate (20 parts)-butyl methacrylate (30 parts) copolymer (B1)

($M_w/M_n=2.8$; $M_n=19000$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=72^\circ\text{C}$.),

to obtain a comparative sample toner.

The offset characteristics of these two toners were examined in the same manner as in Example 1 except that a roller having a surface composed of Daifuron was used as the fixing roller and the fusing temperature was changed to 190 to 200°C . In the case of the comparative sample, occurrence of a conspicuous offset phenomenon was observed, but in the case of the toner sample of this

invention it was confirmed that the offset phenomenon was not caused to occur at all.

Example 5

A toner sample was prepared in the same manner as in Example 4 except that a styrene (50 parts)-methyl methacrylate (20 parts)-butyl methacrylate copolymer (A2)

($M_w/M_n=6.5$; $M_n=9800$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=72^\circ\text{C}$.)

was used instead of the copolymer (A1), Peares 155 was used instead of Dia Black SH (manufactured by Orient Kagaku) and Oil Black BS (manufactured by Orient Kagaku) was used instead of Oil Black BW.

The offset characteristics of the so obtained toner were examined in the same manner as in Example 1 except that the fusing temperature was changed to 210 to 220°C . It was found that the offset phenomenon was not caused at all.

Example 6

A toner sample was prepared in the same manner as in Example 4 except that a styrene (50 parts)-methyl methacrylate (20 parts)-butyl methacrylate (30 parts) copolymer (A3)

($M_w/M_n=8.2$; $M_n=9100$;

B & R= $140 \pm 2^\circ\text{C}$.; $T_g=72^\circ\text{C}$.)

was used instead of the copolymer (A1) MA-8 (carbon black manufactured by Mitsubishi Kasei) was used instead of Dia Black SH and Oil Black BS (Nigrosine dye manufactured by Orient Kagaku) was used instead of Oil Black BW.

The offset characteristics of the so obtained toner were examined in the same manner as in Example 1 except that the fusing temperature was changed to 230 to 240°C . It was confirmed that the offset phenomenon was not caused at all.

Example 7

85 parts of a methyl methacrylate (82 parts)-butyl methacrylate (18 parts) copolymer (A4)

($M_w/M_n=4.2$; $M_n=8500$;

B & R= $135 \pm 2^\circ\text{C}$.; $T_g=85^\circ\text{C}$.)

and 15 parts of the same polystyrene (B) as used in Example 1 were mixed with 4.5 parts of MA-8 and 1.5 parts of Nigrosine Base EX, and the mixture was treated in the same manner as in Example 1, to obtain a toner sample of this invention. The above procedures were repeated similarly by using 10 parts of the copolymer (A4) and 90 parts of

the polystyrene (B), to obtain a comparative toner sample. Resin components of these sample and comparative sample had the following properties.

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Resin of Sample
 $M_w/M_n=3.9$; $M_n=8900$;

B & R= $135 \pm 2^\circ\text{C}$.; $T_g=85^\circ\text{C}$.

Resin of Comparative Sample
 $M_w/M_n=2.7$; $M_n=11500$;

10

B & R= $125 \pm 2^\circ\text{C}$.; $T_g=96^\circ\text{C}$.

The offset characteristics of these two toners were examined in the same manner as in Example 1 except that a roller having a surface composed of FEP was used as the fixing roller and the fusing temperature was changed to 160 to 170°C. In the case of the comparative sample, it was found that the offset phenomena was conspicuous, but in the case of the sample of this invention it was confirmed that the offset phenomenon was not caused at all.

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Example 8

50 parts of the same polystyrene (A1) as used in Example 2 and 50 parts of the same copolymer (A4) as used in Example 7 were mixed with 5 parts of Peares 155 and 2 parts of Nigrosine Base EX, and the mixture was treated in the same manner as in Example 1, to obtain a toner.

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The offset characteristics of the so obtained toner were examined in the same manner as in Example 1 except that a roller having a surface composed of Daifuron was used as the fixing roller and the fusing temperature was changed to 180 to 190°C. It was confirmed that the offset phenomenon was not caused at all.

Example 9

40 100 parts of a styrene (80 parts)-vinyl toluene (20 parts) copolymer (A5)

($M_w/M_n=4.0$; $M_n=1400$;

B & R= $150 \pm 2^\circ\text{C}$.; $T_g=100^\circ\text{C}$.)

45 was mixed with 6 parts of Peares 155 and 2.5 parts of Nigrosine Base EX, and the mixture was treated in the same manner as in Example 1 to obtain a toner sample of this invention. The above procedures were repeated similarly by using instead of the copolymer (A5) a styrene (80 parts)-vinyl toluene (20 parts) copolymer (B2)

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($M_w/M_n=3.3$; $M_n=17000$;

B & R= $150 \pm 2^\circ\text{C}$.; $T_g=100^\circ\text{C}$.)

to obtain a comparative toner sample.

The offset characteristics of these two toners were examined in the same manner as in Example 1 except that the fusing temperature was changed to 190 to 200°C. In the case of the comparative sample, it was found that the offset phenomenon was conspicuous, but in the case of the sample toner of this invention, it was confirmed that the offset phenomenon was not caused to occur at all.

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Example 10

95 parts of a styrene (85 parts)-acrylonitrile (15 parts) copolymer (A6)

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($M_w/M_n=10$; $M_n=8500$;

B & R= $145 \pm 2^\circ\text{C}$.; $T_g=-$)

and 5 parts of poly (methyl methacrylate)

($M_w/M_n=20$; $M_n=3200$;

70

B & R= $145 \pm 2^\circ\text{C}$.; $T_g=-$)

were mixed with 6 parts of Dia Black SH and 2.5 parts of Oil Black BS, and the mixture was treated in the same manner as in Example 1 to obtain a toner sample of this invention. The above procedures were repeated similarly by using instead of the copolymer (A6) a styrene (85 parts)-acrylonitrile (15 parts) copolymer (B3)

75

($M_w/M_n=2.5$; $M_n=22000$;

80

B & R= $145 \pm 2^\circ\text{C}$.; $T_g=103^\circ\text{C}$.)

to obtain a comparative toner sample. The resin components of these sample and comparative sample had the following characteristics:

85

Resin of Sample

$M_w/M_n=11$; $M_n=7800$;

B & R= $145 \pm 2^\circ\text{C}$.; $T_g=103^\circ\text{C}$.

Resin of Comparative Sample

$M_w/M_n=3.3$; $M_n=17000$;

90

B & R= $145 \pm 2^\circ\text{C}$.; $T_g=103^\circ\text{C}$.

The offset characteristics of these two toners were examined in the same manner as in Example 1 except that a roller having a surface composed of Daifuron was used as the fixing roller and the fusing temperature was changed to 190 to 200°C. In the case of the comparative sample, it was found that the offset phenomenon was conspicuous, but in the case of the sample of this invention, it was confirmed that the offset phenomenon was not caused to occur at all.

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Example 11

100 parts of the same polystyrene (A1) as used in Example 2 was mixed with 6 parts of MA-8 and 3 parts of Nigrosine Base EX, and the mixture was treated in the same manner as in Example 1 to obtain a sample A. The above procedures were repeated similarly by further adding 5 parts of Hoechst Wax C (amide wax manufactured by Hoechst Japan), to obtain a sample B. The above procedures were repeated similarly by using 2 parts of zinc stearate instead of the Hoechst Wax C to obtain a sample C.

The offset characteristics of these three samples were examined in the same manner as in Example 1 except that a roller having a surface composed of Daifuron was used as the fixing roll and the fusing temperature was changed to 180 to 190°C. In each of these samples, it was confirmed that the offset phenomenon was not caused to occur at all.

At the pulverizing step of the toner-preparing process, it was found that in the case of samples B and C, occurrence of excessive pulverization was conspicuously reduced as compared with the case of the sample A and excessive pulverization was hardly caused.

Example 12

100 parts of the same copolymer (A2) as used in Example 5 was mixed with 5 parts of Dia Black SH and 2 parts of Oil Black BS, and the mixture was treated in the same manner as in Example 1 to obtain a toner sample A. The above procedures were repeated similarly by further adding 1 part of barium stearate to obtain a toner sample B. The above procedures were repeated similarly by using 4 parts of Plast Flow (ethylene - bis - stearoyl amide manufactured by Nitto Kagaku) instead of the barium stearate to obtain a toner sample C.

The offset characteristics of the so obtained three toner samples were examined in the same manner as in Example 1 except that a roller having a surface composed of FEP was used as the fixing roller and the fusing temperature was changed to 180 to 190°C. In each of these toner samples, it was confirmed that the offset phenomenon was not caused to occur at all. When these toners were used repeatedly, it was found that in the case of samples B and C the frictional charge characteristics were not changed for a longer time than in the case of the sample A and the samples B and C had a longer life than the sample A.

Example 13

95 parts of a styrene (85 parts)-ethylhexyl acrylate (15 parts) copolymer

($M_w/M_n=4.5$; $M_n=11000$;

B & R= $135 \pm 2^\circ\text{C}$; Tg= 74°C .)

and 5 parts of polyvinyl butyral

($M_w/M_n=2.4$; $M_n=23000$;

B & R= $115 \pm 2^\circ\text{C}$; Tg= 62°C .)

were mixed with 6 parts of Peares 155, 1.5 parts of Nigrosine Base EX and 5 parts of Plast Flow, and the mixture was treated in the same manner as in Example 1 to obtain a toner.

The offset characteristics of the so obtained toner were examined in the same manner as in Example 1 except that a roller having a surface composed of FEP was used as the fixing roller and the fusing temperature was changed to 160 to 170°C. It was confirmed that the offset phenomenon was not caused to occur at all.

Example 14

100 parts of a styrene (95 parts)-lauryl methacrylate (5 parts) copolymer

($M_w/M_n=4.6$; $M_n=10000$;

B & R= $135 \pm 2^\circ\text{C}$; Tg= 91°C .)

was mixed with 5 parts of MA-8, 2.5 parts of Nigrosine EX and 5 parts of Hoechst Wax C, and the mixture was treated in the same manner as in Example 1 to obtain a toner.

The offset characteristics of the so obtained toner were examined in the same manner as in Example 1 except that a roller having a surface composed of FEP was used as the fixing roller and the fusing temperature was changed to 170 to 180°C. It was confirmed that the offset phenomenon was not caused to occur at all.

WHAT WE CLAIM IS:—

1. A toner for developing electrostatic latent images comprising a colorant and a main resin based on an α,β - ethylenically unsaturated monomer and having a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) (M_w/M_n ratio) measured as hereinbefore defined of from 3.5 to 40.

2. A toner as claimed in claim 1 wherein M_w/M_n ratio is from 4.0 to 30.

3. A toner as claimed in claim 1 or 2 wherein the number average molecular weight is from 2,000 to 30,000.

4. A toner as claimed in any preceding claim, wherein said resin has a softening point of from 100°C . to 170°C .

5. A toner as claimed in any preceding claim, wherein said resin has glass transition point of from 40°C . to 110°C .

6. A toner as claimed in any preceding claim, wherein said resin is a homopolymer or copolymer of styrene, a substituted styrene,

a vinylnaphthalene, a mono - olefin, a vinyl halide, a vinyl ester, an α - methylene aliphatic monocarboxylic acid ester, an acrylic or methacrylic acid derivative, a vinyl ether, a vinyl ketone, or an N - vinyl compound.

7. A toner as claimed in claim 6 wherein said resin is a homopolymer of an aromatic vinyl compound or an α - methylene aliphatic monocarboxylic acid ester, or a copolymer thereof containing at least 30 mole % of units derived from the aromatic vinyl compound.

8. A toner as claimed in any preceding claim which comprises at least 60% by weight based on total resin, of said main resin and up to 40% by weight, based on total resin of a second resin containing no units derived from an α,β - ethylenically unsaturated monomer.

9. A toner as claimed in claim 8 which comprises at least 75% by weight, based on total resin, of said main resin.

10. A toner as claimed in claim 8 or 9 wherein the second resin is a resin-modified phenol - formaldehyde resin, an epoxy resin, a polyurethane resin, a cellulose resin or a polyether resin.

11. A toner as claimed in any preceding claim wherein the colorant is carbon black, a

nigrosine dye, aniline blue, chalco oil blue, chrome yellow, ultramarine yellow, du Pont oil red, quinoline yellow, methylene blue chloride, phthalocyanine blue, malachite green oxalate, lamp black, rose bengal or a mixture of two or more thereof.

12. A toner as claimed in any preceding claim which comprises from 0.1 to 10 parts by weight, per 100 parts by weight of total resin, of a release agent selected from metal salts of fatty acids, fatty acids having at least 28 carbon atoms, natural and synthetic paraffins, fatty acid esters, partially-saponified fatty acid esters, and alkylene - bis - fatty acid amides.

13. A toner as claimed in claim 12 which comprises from 0.5 to 5 parts by weight, per 100 parts by weight of total resin, of the release agent.

14. A toner as claimed in claim 1 substantially as hereinbefore described with reference to any of Examples 1 to 14.

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